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DEVELOPMENT OF HYDROCARBON ANALYSES

AS A MEANS OF DETECTING LIFE IN SPACE

[2] (NASA Contract No. NASw-508)

(NASA CR-52217)

[redacted]

Principal Investigator:

W. G. Meinschein Oct. 1, 1963

SUMMARY

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ABST

Data have been collected which permit a testing of the hypotheses that the biochemically and chemically least active biological molecules may accumulate unaltered in the elimination products of living things and, in turn, in terrestrial sediments. The concentrations of alkanes in the benzene extracts of cow manure, bat guano, and terrestrial sediments are comparable. These concentrations exceed by more than two orders of magnitude the concentrations of alkanes in the benzene extracts of plants, animals, and a food, butter. Mass spectrometric analyses indicate that alkanes from living things, biological elimination products, and terrestrial sediments are composed of the same types of compounds. Optical activities of hydrocarbons in a crude oil obtained from a 1.1 billion year old sediment have been found to be of the same sign and magnitude as are the optical activities of some relatively young oils.

AUTHOR

[redacted]

INTRODUCTION

Efforts during the third quarter of NASw-508 contract have been directed toward:

1. Modification of the split system on the preparative scale column, and the development of substrates and techniques for the preparative scale separations of alkanes.
2. Developing efficient collectors for the collection of fractions from gas chromatographic columns.
3. Selecting and operating analytical gas chromatographic columns for the fractionation of alkanes.
4. Calibrating and obtaining analyses with the modified Consolidated 21-103C mass spectrometer.
5. "Fingerprinting" of alkanes from biological and sedimental sources.
6. Checking the stability of alkanes in sedimental environments.

STATUS OF RESEARCH PROJECT

The damaged programmer on the Barber-Colman Model 10 gas chromatographic unit has been replaced by the supplier. A specially designed valve, which permits a positive and variable control of the effluent split from preparative scale gas chromatographic columns, has eliminated the difficulty of maintaining the proper split ratio between the detector and the collector exhaust lines.

An efficient collector has been developed for the collection of gas chromatographic fractions. This collector consists of a sintered glass, filter funnel with a sidearm. The bottom end of the funnel is sealed. Powdered dry ice is placed in the funnel and the side arm is connected to the collector tube from the gas chromatographic column. The fraction collects in the bottom of the sealed tube and in the sintered-glass filter. A collected fraction is recovered by rinsing the funnel and decanting the rinse into a sample bottle.

GLC chromatograms have been obtained of alkanes from a variety of ancient sediments. These chromatograms indicate that the distributional patterns of alkanes can be altered in sedimentary environments, but as noted in our preceding Quarterly Report, the distributions of alkanes in some ancient sediments closely resemble the distribution of alkanes in bat guano or cow manure. In certain aspects, the gas chromatograms of alkanes from 20 ancient sediments do retain features observed in the gas chromatograms of biological alkanes, and the distributional variations in ancient sedimental alkane appear to be more a consequence of physical than of chemical processes.

Mass spectrometric analyses have been run on all the sedimental and biological alkane fractions isolated during this investigation.

DISCUSSION

Various hypotheses may be proposed to explain the general compositions of the carbonaceous substances in terrestrial sediments. Barghoorn (1952)[1] and Vallentyne (1962)[2] have discussed the functioning and efficiency of the carbon cycle. Lieth (1963)[3] and Bolin and Keeling (1963)[4] have investigated the exchange of CO_2 between vegetation and the atmosphere.

Based on the quantities of organic substances which probably have been made by living things and the quantities of carbonaceous materials in sediments, it may be deduced that the carbon cycle is extremely efficient. Apparently less than 1 part in a million of biological molecules have escaped the carbon cycle and have been incorporated in an altered or unaltered condition in sediments. Nonetheless, the carbonaceous materials in sediments are distributed more widely and abundantly than are living things. Either in existing or former biospheres certain of these materials may serve as the most ubiquitous biological indicators. In the Quarterly Report of July 1, 1963, for Contract No. NASw-508, reasons were cited why alkanes may be better biological indicators than other carbonaceous substances. This report will discuss considerations which provide a basis for a testable hypothesis on the origins of some liquid and solid alkanes in sediments. Analyses of biological and sedimental alkanes will be presented in support of the hypothesis that is to be developed.

The remarkable efficiency of the carbon cycle may be primarily a consequence of the "biological barrier". Observations of the scavaging and repeated utilization of organic materials by living things as well as examinations of environments that permit a rapid accumulation of organic debris suggest that living things place the principal restrictions on the quantities of carbonaceous substances that are incorporated in sediments.

Studies of sedimentary deposits of various geologic ages show that the formation of carbon-rich sediments were favored by anaerobic conditions which limit microbial activity. Most of the peats, lignites, coals, and related substances in the earth appear to have formed initially in swamps or bogs. Rapid accumulations of organic materials occur almost exclusively in stagnant, aqueous environments where environmental conditions so restrict the numbers of organisms that they cannot consume all the plant and animal remains which are present. In such environments abiotic reactions are provided time to transform biological products into biochemically inert materials. The heats of these reactions may enhance the reaction rates, and the heats as well as the products of these reactions may kill off many of the organisms that try to feed on the organic debris. If it were not for the peat or coal-like deposits that formed in the relatively rare swamp or bog-type environments, the quantities of carbonaceous materials in sediments would be a small fraction of the existing quantities.

In most locations where organisms have lived on earth, only parts per billion of the biological materials formed have apparently been preserved in sediments. Thus, the average biological molecule or the carbon atoms that it contains may have been used millions of times by various organisms. The sequential utilization of organic materials by different living things could be viewed as a fractionation process.

If an analogy may be drawn between this process and distillation, it could be said that the efficiency of the carbon cycle suggests that the biochemical fractionation process is operating under almost total reflux. Consequently, it may be hypothesized that only the biochemically least active biological molecules may accumulate unaltered in sediments and that only the chemically most stable of these molecules can remain unaltered over geologic periods of time.

To test the preceding hypotheses, we have analyzed the benzene extractable carbon compounds in biological samples and in terrestrial sediments. Alkanes or saturated hydrocarbons are the only types of compounds that we have found to be present in significant concentrations in all the samples investigated.

Since the "biological barrier" appears to be the major obstacle to the escape of organic molecules from the carbon cycle, unaltered or altered biological molecules that may accumulate in sediments could be concentrated in the elimination products of living things. Data in Table 1 give the concentrations of alkanes in the benzene soluble fractions of plants and animals, butter, cow manure, bat guano, and terrestrial sediments. A portion of the data in Table 1 were gathered in response to a request by Professor J. R. Vallentyne of Cornell University for these data.

Table 1

Sample Type	Alkane Concentrations in Benzene Soluble Fractions in Per Cent
Living Things(5)*	0.02
Butter(3)*	0.09
Cow Manure(3)*	5.5
Bat Guano(3)*	5.0
Soils(49)*	5.5
Recent Marine Sediments(12)*	6.0

*Numbers in parentheses indicate number of sample analyses that were averaged to obtain the stated per cents.

Tables 2, 3, 4, 5, and 6 present the mass spectrometric analyses of the alkanes from butter, cow manure, bat guano, a Recent marine sediment, and a crude oil from sediments that are 1.1 billion years old. The mass spectrometric type analyses of alkanes from a variety of terrestrial samples are given in Table 7.

The optical activities of alkanes from the 1.1 billion year old oil has been measured by Mr. B. Poczik of O. C. Rudolph and Sons, Incorporated. These measurements and additional pertinent information are:

Instrument: O. C. Rudolph and Sons, Model 80 CSPZA (Calcite Optics).

#600 Mercury Light Source, Micro Devise 3 mm. Simm. Angle ~2-3°, Sample Tube 100 mm. bore 6 mm.

Readings:

Zero point of instrument +0.104.

(Data continued on page 14)

Table 2

Mass Spectrum of Alkanes From Butter

Values in table indicate relative abundances of ions. Positions of values in columns show the masses of ions as may be deduced from the "X" and C numbers at which the values appear. The mass of an ion equals 14 times its C# minus its "X" number. Thus, the peak at the top of the "X" = -3 column at C# = 5 has a mass of 5 x 14 -3 = 67. The masses of ions in a row increase by one unit as do their "X" values from left to right in the table. The masses of ionsin a column increase by 14 units as their C#'s increase by 1 successively down a column. This manner of presenting mass spectral data groups homologous ions within a column.

TOTAL IONIZATION = 67763.00

NORMALIZED ISOTOPE CORRECTED PEAK HEIGHTS (300,000)

"X"→ C#↓	-11	-10	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	+1	+2	C#↓
								0.	0.	-0.	-0.	-0.	-0.	-0.	3
4	-0.	0.	0.	0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	4
5	-0.	0.	-0.	-0.	-0.	-0.	-0.	-0.	2873.	2086.	10613.	5771.	26716.	275.	5
6	124.	102.	90.	109.	223.	122.	718.	701.	4906.	4057.	10678.	3798.	19427.	244.	6
7	67.	131.	96.	76.	392.	147.	988.	889.	5494.	3345.	10972.	2659.	6472.	121.	7
8	106.	83.	72.	73.	370.	202.	1026.	754.	4074.	1992.	6942.	2339.	4536.	101.	8
9	117.	63.	130.	106.	356.	252.	1058.	669.	2992.	1368.	4087.	2025.	3458.	82.	9
10	122.	66.	129.	123.	327.	189.	1173.	596.	2013.	903.	1850.	1667.	2722.	64.	10
11	70.	79.	123.	86.	303.	219.	1335.	554.	1535.	637.	1165.	1412.	2214.	91.	11
12	93.	71.	114.	77.	277.	237.	1179.	439.	1220.	533.	906.	1296.	1914.	66.	12
13	55.	71.	104.	77.	347.	211.	945.	389.	993.	482.	687.	1162.	1711.	73.	13
14	83.	48.	107.	98.	440.	228.	1133.	349.	841.	436.	538.	1093.	1528.	81.	14
15	80.	56.	100.	71.	474.	204.	540.	266.	569.	349.	421.	917.	1338.	79.	15
16	48.	60.	104.	87.	784.	444.	512.	190.	445.	316.	336.	816.	1257.	52.	16
17	64.	30.	126.	78.	404.	317.	412.	182.	406.	279.	290.	728.	1172.	49.	17
18	59.	57.	120.	90.	303.	173.	367.	198.	361.	282.	242.	721.	1113.	117.	18
19	70.	44.	144.	137.	451.	172.	375.	200.	335.	248.	219.	652.	1035.	64.	19
20	52.	56.	114.	84.	266.	138.	246.	194.	287.	259.	236.	583.	954.	70.	20
21	72.	33.	110.	84.	292.	129.	219.	171.	238.	254.	169.	516.	884.	147.	21
22	35.	30.	124.	80.	216.	157.	217.	172.	221.	255.	157.	485.	837.	100.	22
23	43.	42.	107.	86.	200.	136.	193.	181.	191.	242.	131.	450.	748.	246.	23
24	45.	67.	96.	90.	172.	159.	182.	176.	163.	238.	121.	384.	672.	183.	24
25	38.	57.	83.	79.	152.	154.	177.	166.	151.	213.	94.	359.	595.	396.	25
26	39.	60.	112.	76.	221.	150.	138.	170.	117.	198.	92.	306.	500.	166.	26
27	64.	48.	115.	127.	214.	262.	98.	149.	109.	164.	74.	311.	363.	515.	27
28	19.	45.	76.	120.	185.	278.	104.	131.	95.	154.	62.	230.	288.	143.	28
29	21.	43.	64.	163.	126.	279.	76.	125.	65.	145.	33.	212.	213.	713.	29
30	37.	30.	46.	124.	80.	192.	36.	102.	53.	109.	44.	143.	113.	83.	30

Table 3

Mass Spectrum of Alkanes From Cow Manure

Values in table indicate relative abundances of ions. Positions of values in columns show the masses of ions as may be deduced from the "X" and C numbers at which the values appear. The mass of an ion equals 14 times its C# minus its "X" number. Thus, the peak at the top of the "X" = -3 column at C# = 5 has a mass of 5 x 14 -3 = 67. The masses of ions in a row increase by one unit as do their "X" values from left to right in the table. The masses of ions in a column increase by 14 units as their C#'s increase by 1 successively down a column. This manner of presenting mass spectral data groups homologous ions within a column.

TØTAL IØNIZATIØN = 164017.00

NØRMALIZED ISØTØPE CØRRECTED PEAK HEIGHTS (300,000)

"X" → / C# ↓	-11	-10	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	+1	+2	
								0.	0.	-0.	-0.	-0.	-0.	-0.	3
4	-0.	0.	0.	0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	4
5	-0.	0.	-0.	-0.	-0.	-0.	-0.	-0.	9273.	3275.	19562.	5808.	15895.	73.	5
6	276.	774.	313.	670.	3906.	15381.*	3664.	1256.	10884.	3465.	13358.	2726.	10000.	18.	6
7	48.	51.	95.	75.	2280.	445.	2887.	1187.	10272.	2934.	11105.	1453.	2199.	31.	7
8	56.	66.	171.	133.	1195.	339.	2088.	949.	6695.	2020.	6785.	1234.	1573.	31.	8
9	196.	107.	318.	104.	713.	282.	1736.	754.	4362.	1373.	3813.	1186.	1254.	123.	9
10	154.	76.	271.	89.	527.	260.	1798.	706.	2784.	824.	1558.	876.	953.	57.	10
11	96.	52.	218.	81.	448.	240.	1779.	616.	2163.	588.	923.	651.	754.	27.	11
12	68.	38.	159.	70.	443.	232.	1486.	498.	1696.	473.	669.	543.	630.	25.	12
13	54.	34.	130.	65.	449.	226.	1494.	409.	1485.	407.	541.	521.	627.	17.	13
14	53.	30.	130.	71.	534.	222.	1266.	383.	1128.	385.	421.	473.	525.	22.	14
15	56.	45.	149.	97.	560.	206.	800.	285.	771.	325.	331.	377.	426.	22.	15
16	45.	32.	167.	87.	652.	282.	718.	241.	630.	303.	279.	319.	385.	29.	16
17	58.	36.	186.	85.	537.	236.	616.	222.	551.	280.	247.	299.	363.	30.	17
18	70.	40.	206.	84.	427.	184.	557.	222.	501.	265.	223.	270.	349.	51.	18
19	82.	46.	206.	106.	440.	192.	528.	235.	440.	258.	192.	264.	320.	34.	19
20	86.	51.	177.	106.	349.	182.	401.	243.	372.	259.	173.	330.	288.	41.	20
21	80.	64.	155.	116.	320.	208.	327.	240.	296.	255.	135.	199.	246.	49.	21
22	70.	67.	132.	120.	251.	217.	274.	235.	240.	241.	115.	169.	222.	43.	22
23	58.	68.	109.	116.	205.	211.	221.	222.	188.	210.	90.	151.	192.	65.	23
24	52.	64.	91.	116.	156.	199.	179.	208.	139.	182.	67.	122.	151.	41.	24
25	38.	57.	67.	98.	117.	156.	131.	177.	97.	149.	46.	131.	124.	96.	25
26	30.	51.	66.	89.	116.	127.	94.	139.	65.	116.	38.	81.	86.	37.	26
27	80.	49.	57.	90.	98.	153.	68.	119.	49.	93.	26.	88.	69.	91.	27
28	26.	32.	43.	69.	75.	114.	45.	83.	32.	63.	21.	45.	41.	25.	28
29	30.	31.	36.	73.	48.	111.	33.	62.	22.	46.	13.	56.	23.	98.	29
30	16.	61.	20.	56.	24.	71.	20.	46.	11.	32.	7.	20.	13.	11.	30

*Residual benzene solvent.

Table 4

Mass Spectrum of Alkanes From Bat Guano

Values in table indicate relative abundances of ions. Positions of values in columns show the masses of ions as may be deduced from the "X" and C numbers at which the values appear. The mass of an ion equals 14 times its C# minus its "X" number. Thus, the peak at the top of the "X" = -3 column at C# = 5 has a mass of 5 x 14 -3 = 67. The masses of ions in a row increase by one unit as do their "X" values from left to right in the table. The masses of ions in a column increase by 14 units as their C#'s increase by 1 successively down a column. This manner of presenting mass spectral data groups homologous ions within a column.

TØTAL IØNIZATIØN = 19679.00

NØRMALIZED ISØTØPE CØRRECTED PEAK HEIGHTS (300,000)

"X" → / C#	-11	-10	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	+1	+2	C#
								0.	0.	-0.	-0.	-0.	-0.	-0.	3
4	-0.	0.	0.	0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	4
5	-0.	0.	-0.	-0.	-0.	-0.	-0.	-0.	8385.	3806.	19902.	11393.	36844.	0.	5
6	0.	16.	29.	44.	1506.	343.	2719.	963.	8468.	4011.	13896.	4099.	17232.	0.	6
7	0.	0.	32.	13.	1645.	285.	2001.	943.	7377.	3040.	11026.	2200.	3733.	3575.	7
8	1.	36.	119.	81.	831.	232.	1425.	651.	4648.	1645.	6012.	2342.	2744.	6.	8
9	203.	56.	222.	69.	495.	179.	1230.	502.	2887.	1082.	3035.	1338.	1941.	119.	9
10	116.	47.	208.	68.	388.	201.	1272.	575.	1865.	659.	1243.	1459.	1630.	24.	10
11	95.	34.	178.	70.	341.	172.	1242.	427.	1373.	516.	781.	876.	1229.	26.	11
12	64.	37.	147.	72.	355.	196.	993.	324.	1077.	403.	608.	1287.	1210.	41.	12
13	45.	23.	88.	33.	360.	161.	888.	282.	881.	327.	417.	714.	1021.	28.	13
14	47.	23.	103.	45.	404.	181.	1065.	275.	708.	313.	370.	1128.	1101.	29.	14
15	74.	109.	118.	131.	373.	165.	517.	186.	496.	281.	252.	564.	787.	29.	15
16	46.	22.	117.	55.	400.	188.	418.	167.	345.	271.	206.	843.	899.	41.	16
17	9.	12.	150.	63.	428.	132.	349.	176.	342.	237.	178.	480.	760.	62.	17
18	36.	22.	147.	77.	241.	133.	304.	181.	293.	212.	165.	618.	757.	19.	18
19	57.	17.	163.	72.	225.	134.	257.	156.	251.	187.	107.	369.	651.	37.	19
20	39.	51.	79.	73.	195.	138.	178.	155.	175.	186.	92.	463.	596.	85.	20
21	73.	41.	95.	83.	176.	109.	183.	122.	180.	168.	78.	282.	511.	87.	21
22	57.	44.	94.	98.	187.	119.	133.	131.	86.	158.	50.	349.	599.	57.	22
23	14.	39.	65.	73.	101.	140.	83.	142.	83.	127.	56.	363.	424.	139.	23
24	26.	3.	59.	60.	89.	142.	96.	122.	86.	125.	24.	263.	523.	49.	24
25	29.	50.	46.	77.	68.	100.	61.	86.	65.	100.	30.	262.	353.	136.	25
26	9.	52.	45.	46.	76.	83.	34.	63.	26.	81.	21.	234.	526.	67.	26
27	218.	52.	20.	52.	44.	91.	1.	56.	0.	90.	34.	230.	295.	160.	27
28	29.	74.	5.	25.	68.	69.	6.	25.	53.	43.	30.	80.	309.	22.	28
29	70.	51.	10.	55.	12.	54.	12.	24.	22.	53.	12.	115.	114.	140.	29
30	9.	126.	0.	53.	0.	29.	6.	12.	0.	6.	0.	31.	81.	17.	30

Table 5

Mass Spectrum of Alkanes From Recent Terrestrial Sediment

Values in table indicate relative abundances of ions. Positions of values in columns show the masses of ions as may be deduced from the "X" and C numbers at which the values appear. The mass of an ion equals 14 times its C# minus its "X" number. Thus, the peak at the top of the "X" = -3 column at C# = 5 has a mass of 5 x 14 -3 = 67. The masses of ions in a row increase by one unit as do their "X" values from left to right in the table. The masses of ions in a column increase by 14 units as their C#'s increase by 1 successively down a column. This manner of presenting mass spectral data groups homologous ions within a column.

C# ↓ "X" →	-11	-10	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	+1	+2	)
								0.	0.	0.	0.	0.	0.	0.	3
4	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	4
5	0.	0.	0.	0.	0.	0.	0.	0.	8651.	2856.	19270.	4685.	19035.	30.	5
6	0.	66.	75.	99.	1272.	315.	3200.	1239.	11489.	3736.	13919.	2565.	12547.	51.	6
7	42.	76.	110.	52.	1884.	377.	3056.	1409.	12405.	3213.	12392.	1609.	3667.	41.	7
8	30.	64.	135.	141.	1298.	382.	2553.	1163.	7750.	2187.	7827.	1419.	2757.	43.	8
9	188.	103.	336.	132.	900.	358.	2258.	981.	5384.	1625.	4754.	1255.	2179.	129.	9
10	178.	102.	336.	116.	723.	318.	2247.	933.	3561.	1007.	2181.	971.	1766.	78.	10
11	146.	86.	300.	104.	638.	321.	2395.	830.	2329.	778.	1391.	816.	1466.	52.	11
12	112.	52.	233.	87.	578.	300.	2089.	624.	2097.	595.	1150.	723.	1255.	42.	12
13	85.	39.	186.	86.	596.	338.	2147.	800.	1702.	497.	847.	687.	1126.	42.	13
14	74.	35.	186.	60.	738.	327.	2338.	559.	1414.	462.	652.	633.	957.	31.	14-
15	68.	49.	203.	205.	738.	293.	1351.	406.	941.	374.	500.	523.	841.	27.	15-
16	79.	38.	231.	118.	908.	464.	900.	295.	728.	345.	401.	474.	716.	37.	16
17	82.	53.	248.	106.	677.	318.	741.	270.	633.	324.	345.	423.	666.	48.	17
18	99.	49.	296.	118.	539.	256.	678.	281.	579.	316.	291.	412.	609.	52.	18
19	98.	63.	271.	153.	573.	264.	599.	328.	578.	295.	244.	376.	539.	58.	19
20	95.	65.	209.	143.	394.	240.	402.	291.	379.	298.	202.	330.	454.	59.	20
21	86.	67.	182.	130.	368.	212.	327.	243.	308.	265.	163.	276.	405.	53.	21
22	71.	59.	164.	115.	276.	187.	277.	200.	252.	220.	138.	240.	362.	51.	22
23	67.	54.	147.	108.	246.	170.	246.	177.	213.	183.	118.	205.	323.	54.	23
24	57.	54.	126.	102.	210.	107.	233.	164.	187.	162.	100.	152.	298.	47.	24
25	52.	50.	111.	90.	182.	143.	190.	150.	158.	144.	85.	163.	254.	66.	25
26	57.	48.	137.	89.	195.	133.	165.	137.	138.	130.	74.	140.	221.	51.	26
27	56.	69.	212.	133.	202.	172.	148.	127.	121.	119.	66.	123.	182.	94.	27
28	56.	50.	147.	106.	190.	169.	125.	113.	106.	106.	57.	106.	149.	51.	28
29	73.	54.	116.	163.	141.	203.	109.	106.	85.	94.	48.	86.	113.	144.	29
30	39.	57.	103.	131.	94.	145.	86.	89.	71.	77.	40.	68.	83.	39.	30

Table 6

Mass Spectrum of Alkanes From None-Such Crude Oil (Age Approximately 1.1 Billion Years)

Values in table indicate relative abundances of ions. Positions of values in columns show the masses of ions as may be deduced from the "X" and C numbers at which the values appear. The mass of an ion equals 14 times its C# minus its "X" number. Thus, the peak at the top of the "X" = -3 column at C# = 5 has a mass of 5 x 14 -3 = 67. The masses of ions in a row increase by one unit as do their "X" values from left to right in the table. The masses of ions in a column increase by 14 units as their C#'s increase by 1 successively down a column. This manner of presenting mass spectral data groups homologous ions within a column.

TØTAL IØNIZATIØN = 184090.00

NØRMALIZED ISØTØPE CØRRECTED PEAK HEIGHTS (300,000)

C# ↓ "X" →	-11	-10	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	+1	+2	
								0.	0.	-0.	-0.	-0.	-0.	-0.	3
4	-0.	0.	0.	0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	-0.	4
5	-0.	0.	-0.	-0.	-0.	-0.	-0.	-0.	6372.	3511.	20038.	11597.	51642.	0.	5
6	13.	39.	51.	55.	886.	211.	1388.	485.	4512.	5665.	16238.	6438.	33600.	0.	6
7	15.	37.	51.	29.	633.	113.	738.	354.	3458.	2893.	12380.	4132.	6751.	74.	7
8	37.	32.	49.	35.	246.	78.	484.	234.	2015.	1239.	5603.	3540.	4946.	41.	8
9	50.	25.	59.	28.	139.	59.	365.	183.	1212.	656.	2537.	2596.	3591.	34.	9
10	26.	18.	50.	22.	100.	48.	323.	161.	904.	422.	1034.	2034.	2897.	5.	10
11	17.	19.	43.	21.	74.	41.	319.	130.	637.	322.	616.	1702.	2411.	29.	11
12	17.	13.	31.	12.	65.	42.	304.	109.	478.	237.	457.	1458.	2181.	94.	12
13	8.	17.	28.	12.	68.	46.	267.	93.	439.	218.	396.	1326.	2070.	177.	13
14	16.	10.	23.	13.	60.	36.	214.	79.	442.	188.	302.	1085.	1555.	293.	14
15	18.	40.	40.	55.	77.	37.	164.	67.	265.	185.	244.	900.	1343.	336.	15
16	7.	6.	26.	15.	85.	27.	124.	61.	196.	165.	196.	774.	1145.	332.	16
17	5.	6.	36.	11.	72.	29.	112.	58.	183.	144.	172.	664.	986.	306.	17
18	5.	6.	36.	14.	57.	34.	113.	55.	168.	138.	147.	569.	846.	269.	18
19	9.	8.	27.	15.	50.	28.	74.	47.	129.	114.	117.	454.	694.	230.	19
20	8.	5.	21.	10.	35.	18.	60.	43.	110.	102.	94.	353.	548.	184.	20
21	6.	6.	17.	9.	30.	17.	49.	34.	89.	83.	78.	279.	456.	170.	21
22	5.	5.	13.	8.	22.	16.	38.	36.	68.	73.	62.	226.	372.	145.	22
23	5.	0.	7.	5.	18.	12.	36.	25.	63.	58.	48.	180.	296.	121.	23
24	2.	0.	4.	4.	12.	10.	25.	22.	47.	52.	37.	138.	234.	101.	24
25	0.	0.	1.	6.	15.	10.	24.	22.	40.	50.	29.	116.	185.	89.	25
26	4.	3.	7.	8.	12.	12.	17.	21.	32.	37.	25.	86.	137.	68.	26
27	4.	4.	5.	8.	9.	12.	16.	19.	21.	32.	16.	66.	94.	50.	27
28	5.	1.	6.	5.	6.	9.	13.	10.	16.	21.	12.	41.	63.	29.	28
29	1.	3.	2.	6.	5.	6.	9.	10.	9.	18.	7.	26.	40.	18.	29
30	0.	3.	1.	6.	1.	6.	1.	9.	3.	10.	1.	15.	21.	9.	30

Table 7

Mass spectrometric type analyses of the saturated hydrocarbons from crude oils, living things, and Recent and ancient terrestrial sediments. Percentages given for terrestrial samples are averages of the number of samples shown in parentheses to the right of the sample designations. Standard deviations in the per cents of different types of hydrocarbons in the various terrestrial samples are presented to the right of percentage values.

	Per Cents of Saturated Hydrocarbon Types						
		Cycloalkanes					
Sample	Paraffins σ	1-Ring σ	2-Ring σ	3-Ring σ	4-Ring σ	5-Ring σ	6-Ring σ
Living Things(11)*	24.9(6.2)	27.5(2.8)	14.8(1.4)	11.1(2.5)	10.0(2.1)	5.8(2.6)	5.9(2.6)
Cow Manure	16.1	28.5	20.4	14.1	11.4	5.3	4.1
Bat Guano	41.6	26.0	11.4	7.9	6.1	2.5	4.5
Sediments:							
Recent Marine(12)	21.6(6.2)	23.6(2.5)	17.3(2.4)	16.7(1.1)	11.6(1.5)	5.9(1.0)	3.3(0.6)
Ancient(19)	20.6(6.0)	22.2(3.6)	18.5(2.9)	14.7(3.2)	11.8(3.2)	6.2(1.2)	6.1(2.7)
Crude Oils(5)	26.1	28.5	20.2	13.0	7.6	3.5	2.8
1.1 Billion Year Old Crude Oil	63.6	26.2	5.2	2.1	0.9	0.3	1.7

*These samples include oysters, fish, horsemeat, butter, beef, and plants.

Sample	Source Wavelength	Actual	Corrected
Alkanes From None Such Oil	546 mμ	+0.318°	+0.214°
	578 mμ	+0.725°	+0.621°

Concentrations of alkanes in spectral grade iso-octane = 0.396 gm./ml.

$$[\alpha]_{5460}^{35^\circ} = 0.541^\circ$$

$$[\alpha]_{5780}^{35^\circ} = 1.569^\circ$$

Fenske et al (1942)[5] have reported the optical activities of neutral oils (principally alkanes) and of distillate fractions of these oils. Some optical activities found by these investigators are given in Table 8.

Table 8*

Optical Activities of Neutral Oil Fractions With Maximum Rotatory Power

Source of Crude Oil Samples	$\alpha_D^{2^\circ}$
Pennsylvania	+0.25°
Rodessa, La.	+0.79°
Midcontinent #1	+0.93°
Midcontinent #2	+1.20°
California	+2.73°

*From Fenske, M. R., Carnahan, F. L., Beston, J. N., Casper, A. H., and Rescorla, A. R., Ind. Eng. Chem. 34, 638 (1942).

INTERPRETATION OF DATA

Bat guano and cow manure were selected as biological elimination products for the following reasons:

1. Bats consume mainly insects. If alkanes escape the carbon cycle better than other biological compounds, the alkanes from insects or animals would be concentrated in the elimination products of bats.
2. For the preceding reasons, alkanes from plants consumed by cows would be concentrated in cow manure.
3. Both bat guano and cow manure are readily available.

Data in Table 1 indicate that there are comparable concentrations of alkanes in the benzene extracts of cow manure, bat guano, and terrestrial sediments. These concentrations are far greater than the concentrations of alkanes in most benzene extracts of living things or in butter. Interpretations of mass spectra of alkanes of the type shown in Tables 2-6 have been discussed by Meinschein (1957, 1959, 1960, 1961, 1963)[6] and Meinschein, Nagy, and Hennessy (1963).[7]

Mass peaks underlined in Tables 2-6 represent some of the peaks which are commonly larger than peaks above them in their respective "X" columns in the mass spectra of alkanes from living things and sediments. Since in the mass spectrum of an equal molar mixture of all possible hydrocarbons, peaks within each "X" column would probably decrease progressively in size from the top to the bottom of each column. "Anomolous" peaks that are larger than peaks of lower carbon numbers in the same "X" column indicate either the major stable ring systems or the molecular weights of alkanes that are most abundant in the biological and sedimental fractions.

All the peaks underlined in Tables 2-6 are seldom "anomolous" in the spectrum of a specific total alkane fraction. Biological and sedimental alkane fractions appear to be individually unique as do living things. Peaks underlined in the columns from "X" = -11 to "X" = -4 are largest in alkanes that contain high concentrations of cycloalkanes and are smallest in alkanes rich in normal or branched-chain paraffins. Peaks underlined in the "X" = +2 columns contain the parent ions of n-paraffins. These latter peaks are only considered "anomolous" when they are larger than the peaks immediately above and below them. The alternately high and low values of the "X" = +2 peaks in Tables 2-5 in the C_{21} to C_{30} range indicate that odd-carbon numbered n-paraffins in this carbon number range are more abundant than their even-carbon numbered homologs. Alkanes from most Recent sediments and living things that contain in excess of 10 per cent paraffins usually have mass spectra in which some odd-carbon number "X" = +2 peaks are "anomolous", but as reported by Stevens, Bray, and Evans (1956)[8], Meinschein (1957, 1959)[6] and Bray and Evans (1961)[9] these peaks are seldom "anomolous" in crude oils and are only slightly "anomolous" in many ancient sediments. Furthermore, mass spectra of alkanes from certain algae, horsemeat, oysters, and trout obtained in this laboratory and in gorgonians, as reported by Ciereszki, Attaway, and Koon (1963)[10] do not show alternately high and low peaks in the C_{21} to C_{30} range of the "X" = +2 column.

With exception of the peaks underlined in the "X" = +2 columns in Tables 2-6, additional fractionations of biological, sedimental, and crude oil alkanes commonly yield fractions whose mass spectra have anomolous peaks at many of the positions underlined in these Tables (Meinschein 1959, 1961, 1963)[6]. These fractionations concentrate the various types of hydrocarbons that give rise to the "anomolous" peaks, but the mass spectra in Tables 2-6 were obtained on total alkane fractions. An examination of these data show that of the 35 peaks underlined 30, 18, 23, 31, and 18 are "anomolous" in Tables 2, 3, 4, 5, and 6, respectively.

The "anomolies" in Table 6 are much less pronounced than in Tables 2-5 and may be of questionable reliability. Alkanes in the 1.1 billion year old crude oil show some evidence of chemical alterations. The relative sizes of the peaks at 26 and 27 carbon atoms in the "X" = -10, -8, and -6 columns in Table 6 and the low polycyclic alkane content, see Table 7, of the None-Such oil suggest that polycycloalkanes have been altered. But, a relatively small number of young oils and many Pennsylvanian crudes are equally as paraffinic as the None-Such oil. Also, the optical rotatory measurements indicate that the optical activities of the None-Such alkanes exceed those of alkanes from many Pennsylvanian oils (age approximately 250 million years). Since degradations of cycloalkanes would reduce the optical activities of crudes, the optical rotary data presented above do not suggest that the None-Such oil has been extensively altered. Also, the "anomolous" peaks in the mass spectra of alkanes from highly paraffinic oils are not significantly more pronounced than the peaks in the mass spectrum of the None-Such alkanes.

In many mass spectra of alkanes from crude oils, it is observed that if the peak values in an "X" column are plotted against carbon number, inflection points will appear in these plots at the positions where "anomolous" peaks are frequently observed in the mass spectra of biological and sedimental alkanes. These inflection points result because the differences between the underlined peaks and the peak above them are less than the differences between the underlined peaks and the peaks below them. Summing the differences from even- to odd-carbon numbered and from odd- to even- carbon numbered "X" = +2 values in the C_{20} to C_{30} range gives differences of 79 and 96, respectively. This indicates that odd-carbon numbered C_{21}-C_{29} n-paraffins are slightly more abundant in this oil as they are in most crude oils. Similarly, differences between the peaks at "X" = -5 C# = 11, "X" = -6 C# = 27, and "X" = -7 C# = 27 and the peaks above and below each of these peaks show the presence of inflection points.

In addition to the underlined peaks in Tables 2-6 which are frequently observed to be "anomolous" in mass spectra of biological and sedimental alkanes, there are other "features" that can be observed in the mass spectra of these hydrocarbons. Some of these "features" are:

1. Peak sizes in odd-numbered "X" columns decrease more rapidly with increasing carbon number than do peak sizes in even-numbered "X" columns, and in the 18 to 25 carbon number range the even "X" peaks usually approach and subsequently exceed the sizes of odd "X" peaks.
2. Sums of the peaks values of C# 5, 6, and 7 peaks in the "X" = -3, -1, and +1 columns normally exceed one-half the total of the remaining peak values.
3. Plots of peak values versus carbon number for the individual "X" columns with values less than "X" = -5 yield plots with maxima and minima that occur preferential at specific carbon numbers.

Data in Table 7 indicate that the alkanes in cow manure (presumed to be chiefly vegetable hydrocarbons) resemble the alkanes in an average sediment more closely than do the alkanes in bat guano (presumed to be mainly animal hydrocarbons). Compositely the data presented in this Quarterly Review and in our previous Quarterly Review of July 31, 1963, support the hypothesis that alkanes are biochemically and chemically the least active biological molecules. Biological alkanes are apparently concentrated in the elimination products of living things and, in turn, in terrestrial sediments. Alkanes in a 1.1 billion year old sediment have optical activities and distributions that provide evidence of their biological origin.

The None-Such crude oil used in this investigation was supplied by Professor E. S. Barghoorn of Harvard University. Geological information supplied by Professor Barghoorn indicate that it is probable that the oil is as old as the formation in which it is found.

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